EFFECT OF HYDROTHERMAL PRETREATMENT FOR COPROCESSING

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ABSTRACT

We report here effects of hydrothermal pretreatment on coprocessing of three different coals from the Argonne Premium Coal Sample Program. Aqueous pretreatment has resulted in a marked beneficial effect in terms of conversion to hexane solubles for Wyodak subbituminous coal and Zap lignite. The effect on the Illinois No. 6 coal was negligible to slightly detrimental. Hydrothermal pretreatment of Wyodak subbituminous coal (1 part) at 250°, 300°, and 350°C for 30 min followed by coprocessing with Maya ATB (2 parts) at 425°C for 1 h, resulted in 26.0%, 23.5%, and 23.5% hexane insolubles based on total feed. Without hydrothermal pretreatment, 31.5% of the feed ended up as hexane insolubles. Use of a donor solvent, tetralin, in place of water during pretreatment produced 27.5% hexane insolubles, and thus was not as effective as hydrothermal pretreatment for the Wyodak coal. Coupling of phenolic constituents and the effect of water in minimizing such retrogressive reactions provide a possible explanation of these results Support for this hypothesis was found in model compound studies with catechol. We observed that while coupling of catechol on kaolin proceeds very rapidly such that after 3 h at 350°C only 38% of the catechol was recovered, addition of water dramatically mitigated the coupling, with 96% recovery.

INTRODUCTION

The impact of water on coal conversion under different process conditions has been a subject of interest and controversy for some time. Recent studies have shown that mild hydrothermal treatment of an Illinois No. 6 coal substantially enhances conversion into soluble products. For instance the convertibility of an Illinois No. 6 coal into toluene-soluble products increased from ~ 35% to almost 70% when the coal was treated for 30 minutes with water at 250°C under nitrogen, and then subjected to conversion in CO/water systems.(1) Similar favorable effects of mild hydrothermal pretreatment have also been reported for conversions in pyrene (2) and for rapid hydropyrolysis.(3,4) However, the benefits of water pretreatment are clearly not general in that they are not observed for all coals under all combinations of pretreatment and subsequent processing conditions.

We present here results from a study we undertook to determine whether the beneficial effects of mild hydrothermal pretreatment can be exploited in the context of coprocessing. The objectives of this study were to explore the range of benefits, with respect to coal type, temperature of pretreatment, and the manner of water removal. In a parallel study, we have examined the impact of water on clay-catalyzed coupling of phenolics. Together, the two studies strongly indicate that the beneficial impact of water is due to the suppression of retrogressive coupling reactions.

EXPERIMENTAL

The coals used in this study were Wyodak-Anderson seam subbituminous coal, Illinois No. 6 seam high volatile bituminous coal, and Beulah-Zap seam North Dakota lignite; all coals were obtained from the Argonne premium coal bank and used as received. To minimize exposure to air and the time between pretreatment and coprocessing, both the steps were conducted in the same microautoclave. The reactor (43 mL) was charged with approximately 2.25 g of the coal and subjected to pretreatment conditions. Aqueous pretreatment was conducted at 250°, 300°, or 350°C for 0.5 h. After cooling, the excess water was pipetted out. Approximately 4.5 g of Maya ATB was added to the reactor, which was then filled with 1200 psig of hydrogen (cold). The reactor was shaken at 425°C for 1 h in a fluidized sandbath. Before opening the reactor, it was cooled in dry ice to prevent volatiles from escaping. Conversion to hexane solubles was the principal diagnostic used in this study, although other parameters such as THF-solubles, elemental composition, and FIMS-volatility were also determined for selected cases.

RESULTS AND DISCUSSION

Table 1 presents data from the coprocessing studies with Argonne premium samples of Wyodak coal and Maya ATB for a variety of pretreatment conditions. Experiment 1 in Table 1 gives conversion of Maya alone with no coal added and Experiment 2 gives the result for coprocessing without any pretreatment. These entries represent base-line values to be used for determining the effect of various pretreatments shown in subsequent lines. Using the baseline conversion of Maya alone, we can determine the theoretical conversions of coal assuming that there is no interaction between the coal and and resid. For instance, 18% by weight of hexane insoluble (HI) material was obtained after treating Maya under these thermal coprocessing conditions. If coal were added (in a ratio of 1 part coal to 2 parts Maya), then we would have obtained a yield of 12% if all of the coal had been converted to hexane soluble material. In contrast, if none of the coal had been converted, a value of 45% insoluble material would have been obtained. As shown in the table the results ranged from 22 to 34% hexane insoluble material, indicating that a significant portion of the coal had been converted.

Effect of Pretreatment Conditions on Coprocessing of Wyodak and Maya ATB

From the data in Table 1 we can immediately see that there is a marked beneficial impact of hydrothermal pretreatment with the yield of hexane-insolubles being reduced from 32% without pretreatment to 26% with pretreatment at 250°C (Experiments 3 and 4). Hydothermal pretreatment at 300°C further reduces hexane-insolubles yield to 24%. Increasing the pretreatment temperature to 350°C results in no further benefit in terms of conversion to hexane-solubles. The additional conversion is not merely due to the extra heating that pretreatment provides. Dry heating of coal for 30 min at 350°C prior to coprocessing is in fact deleterious and results in 34% hexane-insolubles. Even thermal pretreatment in tetralin, a donor solvent, is not as beneficial as hydrothermal pretreatment.

Baldwin et al. have shown that mild pretreatment treatment of several coals with with acidic alcohol solutions results in enhanced conversion during subsequent coprocessing.(5) The premise of their work was that the pretreatment alkylates the coals thus preventing the phenolic and carboxylic groups from undergoing retrogressive reactions and lowering the yields. However, another possibility is that the pretreatment actually dewatered the coal, and the removal of water under mild conditions aided in the enhanced conversions. To test this hypothesis we used acetone which is also completely miscible with water, but which cannot alkylate hydroxyls. However, this treatment was somewhat deleterious and resulted in a slight increase in hexane-insolubles: 34% compared to the base line case of 33%.

To determine if the pretreatment effect was limited to the coal, we treated the Maya ATB at 350°C in water. The water was removed, and Maya ATB was then subjected to treatment at 425°C in nitrogen (Experiment 15) and in hydrogen (Experiment 16). In both cases the conversion was no different from that of no pretreatment. The fact that the HI yields under nitrogen and hydrogen for pure Maya are the same is interesting, and suggests that perhaps the upgrading of the Maya is primarily a disproportionation reaction, where the hydrogen utilized for the upgrading comes directly from the Maya ATB itself. This conclusion is in concert with the findings of Savage et al., (6) and Khorasheh et al.(7) who have reported that presence of hydrogen does not increase the yield of the distillates (which is often equated to hexane-solubles) under thermal and catalytic processing of resids and gas oils, although it reduces coke formation.

Effect of Coal Rank on Hydrothermal Pretreatment

Table 2 presents data from the coprocessing studies with Argonne premium samples of Wyodak, Illinois No. 6, and North Dakota coals and lignite. Although bituminous coals are generally more easily converted than subbituminous coals, coprocessing of Wyodak and Illinois No. 6 coals without pretreatment led to about the same extent of conversion, yielding 32-34% hexane-insoluble material. However, although the pretreatment of Wyodak gave a significant enhancement of conversion, no benefit for the Illinois No. 6 coal was observed. Hydrothermal pretreatment of the lignite at 350°C was moderately beneficial. It should be remembered that we had optimized the pretreatment conditions using the Wyodak coal; and *a priori* have no reason to assume that these conditions are optimal for other coals as well. The lignite may show a more pronounced effect with a lower temperature hydrothermal pretreatment. Nevertheless, these results show that the beneficial effects of hydrothermal pretreatment are not specific to the Wyodak coal and that other low rank coals also show qualitatively similar enhancement in conversion.

Possible Chemical Basis for Hydrothermal Pretreatment

Various factors could explain the phenomenon of hydrothermal pretreatment and how it relates to the ultimate convertibility of coal. One possibility is that morphologogical changes affect mass transfer rates because the water contact increases pore volume and therefore opens the coal structure for subsequent conversions. However, other, more chemical explanations must also be considered. Because the impact of hydrothermal pretreatment was generally more pronounced for low rank coals, which have relatively large amount of dihydric phenols, and because dihydric phenols are particularly prone to coupling reactions, we investigated the effects of mineral/organic interactions by use of model phenol systems such as phenol and catechol, and mineral systems such as montmorillonite and kaolinite. In previous work we have shown that unless H-donor solvents are present, phenolics such as catechol and resorcinol undergo rapid coupling reactions (8). Trewhella et al., have also reported that the presence of hydrogen donors such as tetralin significantly reduces the polymerization of phenolic compounds to larger ring furans (9).

We conducted a series of experiments in which catechol was heated in a sealed quartz ampoule in the presence of kaolin, a common clay mineral found in coals, and in the presence or absence of water or tetralin. Under the experimental conditions a substantial amount of catechol was converted to polymeric materials and not recovered. The product mixture was analyzed by GCMS to determine the amount of unconverted catechol and the small yields of phenol. Table 3 presents data on the self-coupling reactions of catechol in the temperature range from 300° to 400°C, and how it is modified by kaolin, tetralin, and water. As shown in this table, only a small amount of the catechol underwent any condensation reactions when heated by itself to 400°C for 1 h (Experiment 1). It remained essentially as catechol (75%) or phenol (18%) with only 7% of material unaccounted for. Reaction at 350°C (Experiment 4) results in even less of coupling products. However addition of kaolin markedly accelerated coupling reactions. For instance, after 3 h at 350°C a mixture of catechol and kaolin (Experiment 5) contains only 46% of the original catechol (and 4% phenol), compared to 92% and 1% with no clay added (Experiment 4). Addition of water, on the other hand, results in inhibition of these coupling reactions. In Experiment 6 water was added to the mixture, and 89% of the catechol was recovered, and 1% phenol was formed. Analogous effects of clay and water were observed at 400°C. Addition of clay promotes coupling of catechol with only 2% of the catechol being recovered (Experiment 2), while in the presence of water, 84% was recovered (Experiment 3). These results are very interesting, and suggest that pretreatments and/or conversions in the presence of water should minimize crosslink formation by phenols of this type and lead to larger yield and/or a better quality product.

CONCLUSIONS

We have shown here that hydrothermal pretreatment of low rank coals enhances conversion to hexane-solubles during subsequent coprocessing. We further showed that for the Wyodak coal, the benefit increased from an increase in the pretreatment temperature from 250° to 300°C, but no additional benefits were derived by further increase of temperature to 300°C. Dry thermal pretreatment is deterimental and even thermal pretreatment in donor solvents is not as effective as aqueous pretreatment. We suspect that some of the benefits seen here evolve from changes brought about in clay-promoted retrogressive condensation chemistry. In a small study conducted to understand this phenomena we have shown that water markedly attenuates the clay-catalyzed coupling of phenolics.

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Table 1

COAL CONVERSION FROM COPROCESSING MAYA ATB AND WYODAK COAL IN MICROAUTOCLAVE[a]

Experiment	Pretreatment[b]	HI (wt%)	Coal Conversion[b]
1	Maya (no coal)	18	--
2	None	32	40
3	250 °C	26	53
4	250 °C	27	53
5	300°C	23	66
6	300°C	24	63
7	350°C	22	69
8	350°C	25	60
9	Thermal 350°C	34	33
10	Thermal 350°C	34	33
11	Vac Dried 56°C	34	33
12	Acetone Dried	33	36
13	Tetralin 350°C	28	52
14	Tetralin 350°C	27	55
15	Maya (no coal, 350 pret)	20	--
16	Maya (no coal, 350 pret)	23	--

a. Reactions of coal and Maya ATB at 425°C for 1 h at and 1200 psi H_2. HI refers to Hexane insoluble fractions.

b. Coal conversion calculated assuming that the insoluble material from the Maya remains the same during the coprocessing experiment.

Table 2

COPROCESSING OF COALS OF DIFFERENT RANK WITH MAYA ATB IN MICROAUTOCLAVE[a]

Experiment	Coal	Pretreatment	Hexane Insoluble	Coal Conversion[b]
1	None	None	18	--
2	Wyodak	None	32	40
3	Wyodak	350°C	22	69
4	Wyodak	350°C	25	61
5	Illinois No. 6	None	34	33
6	Illinois No. 6	350°C	35	30
7	Lignite	None	28	52
8	Lignite	350°C	24	64

a. Reactions of coal and Maya ATB at 425°C for 1 h at and 1200 psi H_2.
b. Coal conversion calculated assuming that the insoluble material from the Maya remains the same during the coprocessing experiment.

Table 3.

EFFECT OF WATER ON CLAY-CATALYZED COUPLING REACTIONS OF CATECHOL

				Mass Balance (Mol%)		
Run	Description	Temp (°C)	Time (h)	Catechol	Phenol	Remainder
1	Catechol	400	1	75	18	7
2	Catechol/ Kaolin	400	1	2	0.2	98
3	Catechol/ Kaolin/water	400	1	84	3	13
4	Catechol	350	3	92	1	7
5	Catechol/ Kaolin	350	3	38	4	52
6	Catechol/ Kaolin/water	350	3	89	1	10
7	Catechol/ Kaolin	300	5	83	8	9
8	Catechol/ Kaolin/water	300	5	99	0	0